



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Low temperature oxidation of plutonium

A. J. Nelson, P. Roussel

January 31, 2013

Journal of Vacuum Science and Technology A

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Low temperature oxidation of plutonium

A. J. Nelson^{a) b)}

Lawrence Livermore National Laboratory, Livermore, California 94551

P. Roussel

AWE, Aldermaston, Reading, Berkshire, U. K. RG7 4PR

^{a)}American Vacuum Society member.

^{b)}Electronic mail: nelson63@llnl.gov

The initial oxidation of gallium stabilized δ -plutonium metal at 193 K has been followed using X-ray Photoelectron Spectroscopy. On exposure to Langmuir quantities of oxygen, plutonium rapidly forms a trivalent oxide followed by a tetravalent plutonium oxide. The growth modes of both oxides have been determined. Warming the sample in vacuum the tetravalent oxide reduces to the trivalent oxide. The kinetics of this reduction reaction has been determined to be 38.8 kJmol^{-1} .

I. INTRODUCTION

The corrosion of plutonium is a topic of continuing interest and is an important consideration in establishing procedures for safe handling and storage of this radioactive and toxic material. Plutonium is a highly oxophilic metal and typically exists with an oxide film even in the stringent conditions of a high quality inert gas glove box. The oxidation of plutonium metal initially occurs via a trivalent sesquioxide followed by the

tetravalent dioxide [1]. There are no higher oxidation state oxides formed in the solid state, which is not the case for the lighter actinides (Pa - Np). The oxidation of plutonium is further complicated as the tetravalent dioxide is thermodynamically unstable with respect to the metal and will reduce to the trivalent oxide in reducing environments i.e. vacuum [2]. A two dimensional layered model of plutonium oxidation was proposed and examined using Ultraviolet Photoelectron Spectroscopy (UPS) by Butterfield *et al.* [3] This is a simplistic model which has been used to determine the activation energy for the reduction of the tetravalent dioxide to trivalent oxide using X-ray Photoelectron Spectroscopy (XPS) by Morrall *et al.* [4] More recently sub-stoichiometric trivalent oxide $\text{Pu}_2\text{O}_{3-y}$ has been detected using XPS as reported by García Flores [5].

The term low temperature oxidation is typically used to describe at or below room temperature corrosion. At low temperatures a thin oxide film rapidly forms as the activation energies are very small, typically growing to a limiting thickness [6]. Low temperatures limit diffusion processes of the migrating species. This would have the benefit of enabling investigation of the forward oxidation reaction of plutonium without the competing reduction of Pu^{4+} to Pu^{3+} oxide reaction. Indeed, García Flores *et al.* have reported temperatures above 260 K to enable the reduction of Pu^{4+} oxide [7]. Furthermore, the growth modes of the oxidation reaction can be determined from the quantification of the adsorbate-substrate ratio as a function of gas exposure [8].

In this present investigation, XPS is used to follow the initial stage of low temperature oxidation. The Pu 4f photoelectron spectra are critically evaluated to determine the growth mode of the oxide films, then allowing the sample to warm up to

enable ion diffusion of the migrating species and following the reduction of tetravalent to trivalent plutonium.

II. EXPERIMENTAL

XPS measurements were made using a Physical Electronics 5400 spectrometer employing achromatic Al K α X-ray source (1486.7 eV) operating with a base pressure of 1×10^{-9} torr. All measurements were made with the sample surface normal to the electron analyzer unless otherwise stated. Spectra were acquired using a 0.2 eV step size and a pass energy of 35.75 eV. No additional gains in spectral resolution were found acquiring spectra at lower pass energy values. Angle dependant XPS measurements were acquired between 0 and 45 ° of the surface normal with respect to the electron analyzer.

The sample consisted of a gallium δ -stabilized alloy and was electro-polished before mounting. The sample was moved into the ultra high vacuum system of the XPS spectrometer and following the transfer it was noted the surface had tarnished from a silver metallic luster to an orange-brown coloration. In the UHV chamber the sample was subjected to 4.5 kV argon ion sputtering to remove any oxide contamination and tarnished discoloration. Prior to any gas dosing experiments the sample was further cleaned by Ar ion sputtering until there was no detectable signal attributable to O 1s and C 1s regions at a pass energy of 35.75 eV. The sample was not subjected to any annealing treatments.

The core-level spectra were curve fitted using CASA XPS software. After fitting a Shirley background (406-459 eV) the X-ray induced satellites were mathematically subtracted from the raw data. Unconstrained peak fitting on up to twenty three

independent spectra for each of the separate oxidation states of the Pu^{4+} oxide, Pu^{3+} spectra and Pu^0 metal afforded a statistical analysis of the peak position, FWHM and shake up satellite to main peak ratios. Constraints were applied to each oxidation state fit so that the intensity of these species could be consistently and reproducibly evaluated and compared. The curve fits for each oxidation state were found to be identical to those previously reported [7]. Following curve fitting the intensities were corrected for atomic concentration and density. The inelastic mean free path was calculated using the TTP2 equation [9].

Ambient temperature X-ray diffraction measurements were acquired using a Siemens D5000 diffractometer operating in a Bragg-Brentano geometry employing $\text{Cu K}\alpha$ radiation and a Miostar position sensitive detector. Patterns were collected between $20\text{--}120^\circ 2\theta$ with a step size of $0.01^\circ 2\theta$. The main mechanical assembly of the diffractometer is mounted in a nitrogen filled glove box operating typically with $\text{H}_2\text{O} < 5$ ppm and $\text{O}_2 < 1\%$ by volume.

III. RESULTS AND DISCUSSION

During cooling to 193 K the sample was cleaned using Ar ion sputtering. Prior to any gas dosing experiment the sample surface was checked for cleanliness (Bottom spectra in Figure 2). The peaks attributable to the $\text{Pu } 4f_{7/2,5/2}$ spin orbit pair showed the typical asymmetric line shape with the distinct shoulder at about 2 eV to higher binding energy. The shoulder to high binding energy has been accredited to localization of the 5f electrons in δ -Pu phase [10]. Throughout the following discussion this high binding energy shoulder has been interpreted as oxide impurity from the experimental evidence

now discussed. First, the high binding energy shoulder occurs at the position for Pu^{3+} oxide. Secondly, the Pu 4f peaks are significantly more sensitive to oxide impurity compared to O 1s signal due to the higher Relative Sensitivity Factor (RSF). Thirdly, the intensity of the shoulder relative to the main peak varies from sample to sample and sometimes varies between sputtering cycles on the same sample, which is an indication of surface contamination, in contrast to thorium. The high binding energy peaks in the Th 4f spectrum do not vary in intensity relative to the main spin orbit doublet and are attributed to the localization of screening orbitals [11]. Fourthly, similar to other studies, undertaking grazing incidence XPS measurements increases the intensity of the higher binding energy shoulder relative to the main photoemission peaks thus showing that it is surface related [10, 12, 13]. Finally, although no O 1s signal can be detected using a pass energy of 35.75 eV, a small peak is detectable when increasing the pass energy to 178.95 eV (Figure 1).

Carbon is a ubiquitous impurity in plutonium metal and is often incorporated at the time of casting. The inclusion of small amounts have been shown to effect oxide stoichiometry in plutonium corrosion films [7] and also corrosion mechanisms in both thorium [14, 15] and uranium [16]. The C 1s spectra are also included in Figure 1 at both pass energies of 35.75 and 178.95 eV. Interestingly there is little difference between the two spectra at different pass energies when normalised and no peak attributable to C 1s to the limits detectable by XPS. Both spectra show a very broad peak encompassing the whole spectral window. This broad peak is attributable to the Pu $5p_{1/2}$ photoemission line [7]. The absence of any detectable carbon impurity in this sample is of significance in understanding plutonium corrosion.

The sample was exposed to increasing Langmuir quantities of oxygen at 193 K. The Pu 4f peak shape rapidly changed to that attributable to Pu³⁺ followed by a change to the Pu⁴⁺ peak shape (Figure 2). The oxidation appeared to stop when the quantity of Pu⁴⁺ reached about 50% after exposure to 53 L of oxygen. Concomitantly, the O 1s intensity (not shown) rapidly increased up to exposures of 53 L and then did not change. No attempt has been made to quantify the Pu 4f to O 1s ratio within this work as there are multiple values reported for the RSF for Pu 4f [7, 17, 18, 19] and this may introduce possible confusion in the data analysis. The changes to the Pu 4f spectra were similar to those reported for the room temperature oxidation, however, the higher temperature involved in those studies allowed diffusion to occur and afforded a greater quantity of the Pu⁴⁺ oxide as evidenced from the peak shape [20]. Finally, there was no evidence of the reduction of Pu⁴⁺ to Pu³⁺ oxide phase in UHV at this lower temperature.

The concentration ratio of the metal and the two oxides are shown in Figure 3. The rapid growth of the Pu³⁺ adsorbate phase and associated fast decrease in the Pu⁰ metal substrate signal are typical of a two dimensional layer by layer growth mode also known as the Frank-van der Merwe growth type [8]. Therefore the film thickness was calculated from the method described by Hill *et al.* [21] and the results are shown in Figure 4. A linear regression fit to a plot of (Pu³⁺ film thickness)² verses oxygen exposure afforded an R^2 value of 0.9974, which demonstrates the growth of the Pu³⁺ film is parabolic up to thickness until the Pu⁴⁺ oxide phase starts to form. Mott and Cabrera explained the parabolic growth kinetics of initial low temperature oxidation as ion movement through the film being the rate limiting step and oxidation is driven by the tunneling of electrons from the metal to the oxide-gas interface [6, 22].

The Pu⁴⁺ oxide phase starts growing in at exposures between 18-34 L of oxygen where there is diminishing contribution to the Pu 4f spectrum from the Pu⁰ metal peak shape. In the current work the initial fast growth of the Pu⁴⁺ oxide phase rapidly slows down to almost no further oxidation when at 50 % of the contribution to the Pu 4f spectrum and no Pu⁰ metal peak shape can be detected. Comparison of the Pu⁴⁺:Pu³⁺ ratio with the mathematical models of the growth modes reported by Ossicini *et al.* show that it can be island growth, Volmer-Weber or island on layer growth called Stranski-Krastanov growth with the latter being the more common growth mode [8, 23]. Further support for an island growth mode was determined from the grazing incidence XPS measurements. These show the increase in the Pu⁴⁺ intensity at the loss of the Pu³⁺ intensity with increasing angle. This confirms that the Pu⁴⁺ oxide phase is indeed located on the surface. After evaluating the data using the film thickness method described by Hill, a linear regression fit to a plot of $\ln(1 + I_{\text{Pu}^{4+}} / I_{\text{Pu}^{3+}})$ versus $1/\cos(\text{angle})$ showed that it did not pass through the origin, which would be required for a Frank-van der Merwe growth mode thus confirming island growth. The formation of the Pu⁴⁺ oxide is similar to thorium, which has been reported to form ThO₂ at 37 L exposure and occur via an island growth mode [14, 15]. This similarity with Th⁴⁺ that has a closed shell electronic configuration may occur as the 5f electrons in plutonium become sufficiently localized so no further reaction can occur.

Now that the oxidation reaction has been examined, we turn to the reduction reaction. Upon warming the sample above 233 K in UHV, the reduction of Pu⁴⁺ to Pu³⁺ was observed to occur and the reaction kinetics were followed (Figure 5). A plot of the reaction profile showed this reaction was decelerating. This is indicative of a diffusion-

controlled reaction [24]. It was difficult to control the sample temperature and acquire suitable quality data when raising the temperature from below 233 K to temperatures above 253 K. Therefore an alternative approach to follow this reaction at a range of temperatures was taken. The sample was exposed to 5000 L of oxygen at 268 K while constantly cooling the sample. This typically afforded a mixed Pu^{3+} , Pu^{4+} oxide with the quantity of Pu^{4+} oxide > 70 %. The sample was then taken to the desired reaction temperature ± 1 K and the reaction was followed. The data were modeled using a one dimensional diffusion model [24]. A linear regression fit to an Arrhenius plot afforded an activation energy of 38.8 kJmol^{-1} . This value was surprisingly low when compared to the value of 75 kJmol^{-1} reported earlier [4]. However, it should be noted that the earlier study calculated the activation energy from a single temperature diffusion measurement using the assumption reported by Mukherjee *et al.* [25].

The oxides phases have been described using the formal oxidation state in this work as it had not been determined if the oxide was crystalline or amorphous. A sample of δ -stabilized Pu was electropolished to a silvery metallic luster and immediately mounted on the goniometer stage for XRD analysis. The sample remained mounted on the stage in excess of 40 days and patterns were acquired at timely intervals. During this time the sample surface tarnished to an orange brown coloration. There was no difference in the XRD pattern acquired within an hour of electropolishing and after 42 days. This means the tarnished oxide is either below the detectable limits of XRD or is amorphous. Larson and Cash used ellipsometry to characterize the colors of plutonium oxide thicknesses and reported a similar color to be 40 nm thick [26]. A 40 nm thick

crystalline oxide should be easily detectable using XRD [27]. This work suggests the initial thin oxide grown on plutonium at room temperature is amorphous.

IV. SUMMARY AND CONCLUSIONS

The oxidation of plutonium has been studied at 193 K with core-level photoelectron spectroscopy. XPS results reveal that the Pu^{3+} oxide phase grows rapidly following a 2-D Frank-van der Merwe mode. This was followed by the growth of the Pu^{4+} oxide by an island growth mode (Stranski-Krastanov). At this lower temperature the oxide growth was found to slow down when the Pu^{4+} oxide reached 50 % quantity. The activation energy for the reduction of Pu^{4+} to Pu^{3+} oxide was measured to be 38.8 kJmol^{-1} . Finally, XRD results indicate that the oxide formed at room temperature over a period of 40 days appears amorphous.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U. S. Dept. of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344.

References

1. J. M. Haschke, T. H. Allen, L. A. Morales, Los Alamos Sci. **26**, 252 (2000).
2. J. C. Martz, J. M. Haschke, J. L. Stakebake, J. Nucl. Mater. **210**, 130 (1994).
3. M. T Butterfield, T. Durakiewicz, E. Guziewicz, J. J. Joyce, A. J. Arko, K. S. Graham, D. P. Moore, L. A. Morales, Surf. Sci. **271**, 74 (2004).
4. P. Morrall, S. Tull, J. Glascott, P. Roussel, J. Al. Compds. **444-445**, 352 (2007).
5. H. G. García Flores, D. L. Pugmire, IOP Conf. Series: Mater. Sci. Eng. **9**, 012038 (2010).
6. N. Cabrera, N. F. Mott, Rept. Prog. Phys. **12**, 163 (1948-49).
7. H. G. García Flores, P. Roussel, D. P. Moore, D. L. Pugmire, Surf. Sci. **605**, 314 (2011).
8. C. Argile, G. E. Rhead, Surf. Sci. Rep. **10**, 277 (1989).
9. S. Tanuma, C. J. Powell, D. R. Penn, Surf. Interface Anal. **21**, 165 (1994).
10. L. E. Cox, Phys. Rev. B **37**, 8480 (1988).
11. J. C. Fuggle, M. Campagna, Z. Zolnierrek, R. Lasser, A. Platau, Phys. Rev. Lett. **45**, 1597 (1980).
12. L. E. Cox, O. Eriksson, B. R. Cooper, Phys. Rev. B, **46** 13571 (1992).
13. P. Roussel, D. S. Shaw, D. A. Geeson, J. Nucl. Sci. Tech. Supplement 3, 78 (2002).
14. W. McLean, C. A. Colmenares, T. L. Smith, G. A. Smorjai, Phys. Rev. B **25**, 8 (1982).
15. M. Bagge-Hansen, R. A. Outlaw, M. Y. Zhu, D. M. Manos, Surf. Interface Anal. **43**, 1192 (2011).
16. W. P. Ellis, Surf. Sc. Lett., **109**, L567 (1981).
17. T. Gouder, L. Havela, Mikrochim. Acta, **138**, 207 (2002).
18. P. Morrall, P. Roussel, L. Jolly, A. Brevet, F. Delaunay, J. Nucl. Mater. **385**, 15 (2009).
19. D. T. Larson, J. M. Haschke, Inorg. Chem., **20**, 1945 (1981).

20. D. T. Larson, J. Vac. Sci. Technol., **17**, 55 (1980).
21. J. M. Hill, D. G. Royce, C. S. Fadley, L. F. Wagner, F. J. Grunthaner, Chem. Phys. Lett., **44**, 225 (1976).
22. A. T. Fromhold, Fundamental Theory of Metal Oxidation (North-Holland, Amsterdam, 1976).
23. S. Ossicini, R. Memeo, F. Ciccacci, J. Vac. Sci. Tech. A, **3**, 387 (1985).
24. S. Vyazovkin, A. K. Burnham, J. M. Criado, L. A. Perez-Maqueda, C. Popescu, N. Sbirrazzuoli, Thermochim. Acta, **520**, 1 (2011).
25. A. Mukherjee, S. P. Wach, J. Less Common Met., **92**, 289 (1983).
26. J. M. Haschke, Los Alamos Report LA-13296-MS (1997).
27. R. J. Jackson, R. J. Pinkney, Metallography, **1**, 387 (1969).

Figure Captions

Figure 1. O 1s spectra (left), C 1s spectra (right) of sample after sputter cleaning. Bottom spectra were acquired using a pass energy of 37.75 eV, top spectra were acquired using a pass energy of 178.95 eV.

Figure 2. Evolution of Pu $4f_{7/2,5/2}$ spectra as a function of oxygen exposure in Langmuirs. X-ray induced satellites have been removed for clarity.

Figure 3. Plutonium oxidation state concentration as a function of gas exposure.

Figure 4. Parabolic Pu³⁺ film thickness growth for as a function of gas exposure.

Figure 5. The reduction of Pu⁴⁺ to Pu³⁺ in UHV at 283 K. X-ray induced satellites have been removed for clarity.

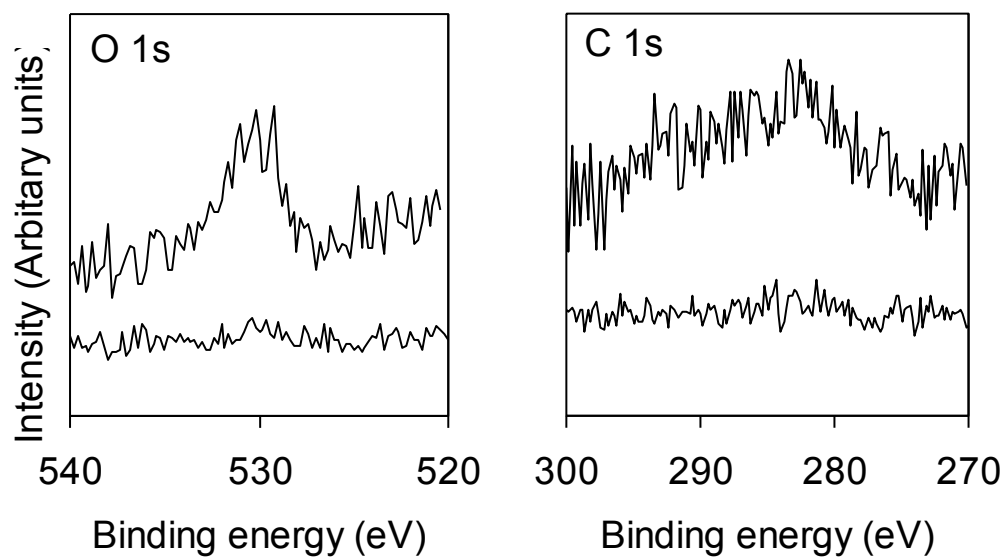


Figure 1.

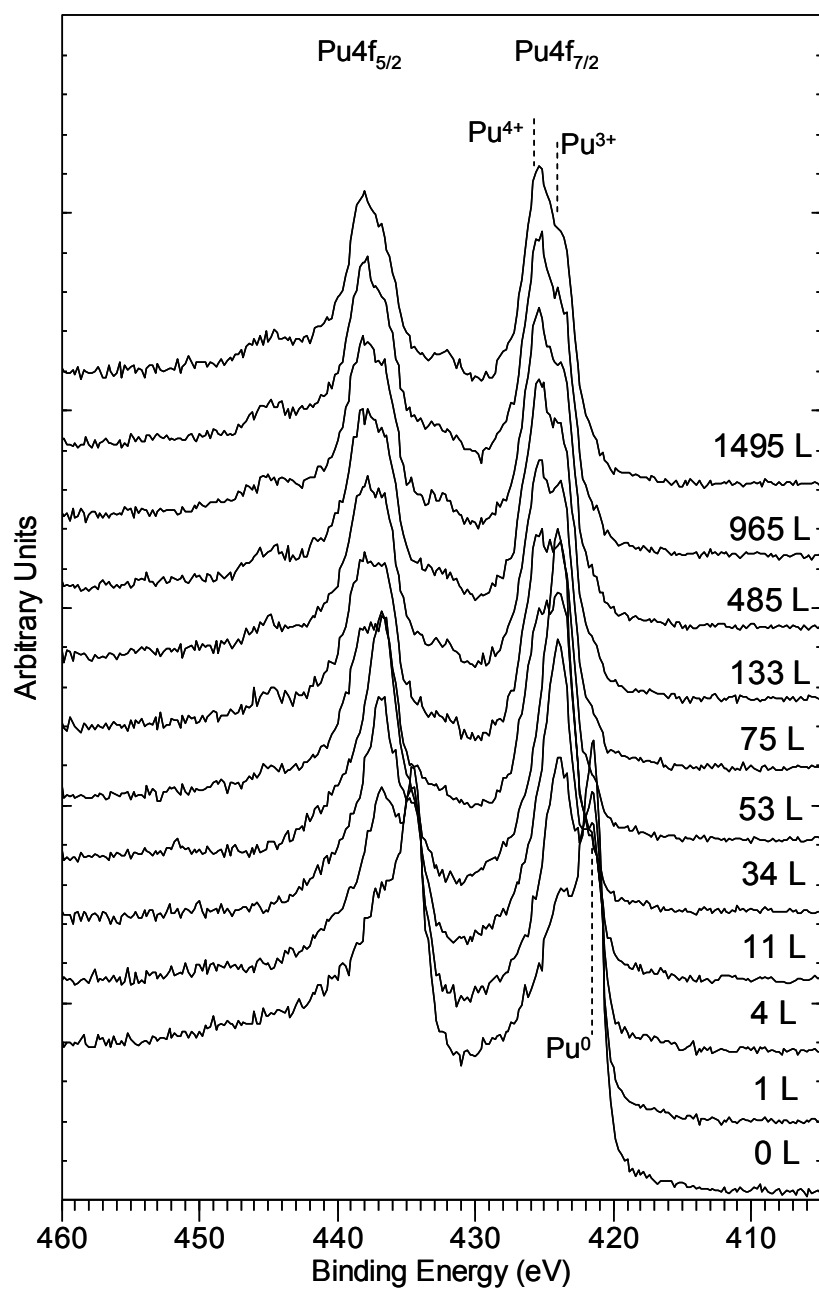


Figure 2

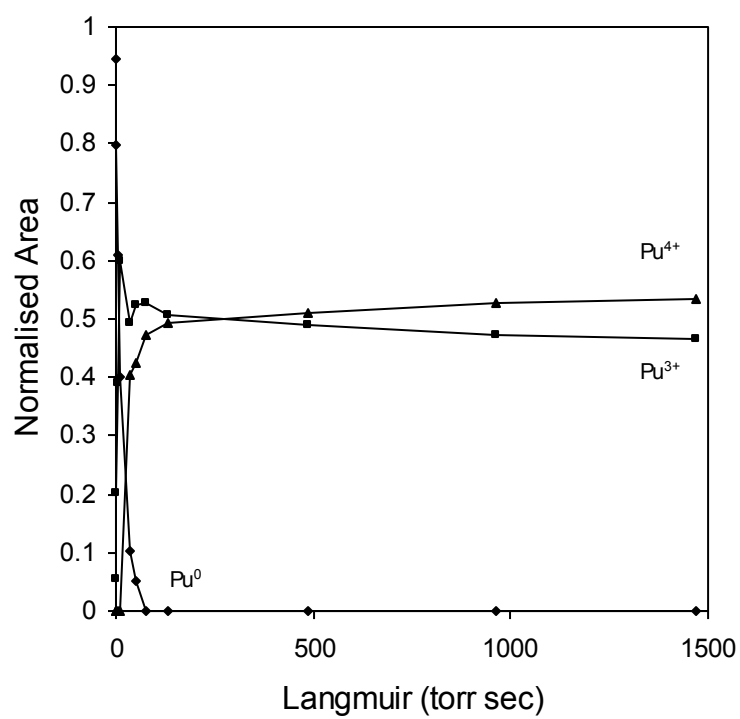


Figure 3

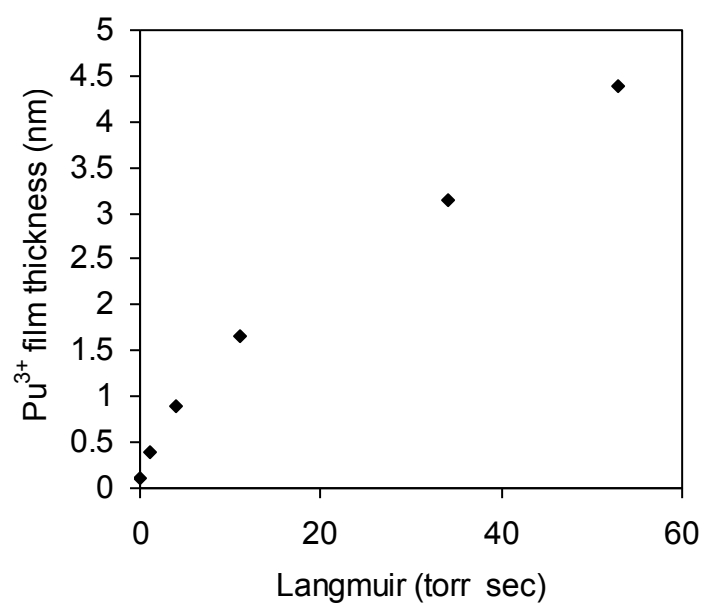


Figure 4

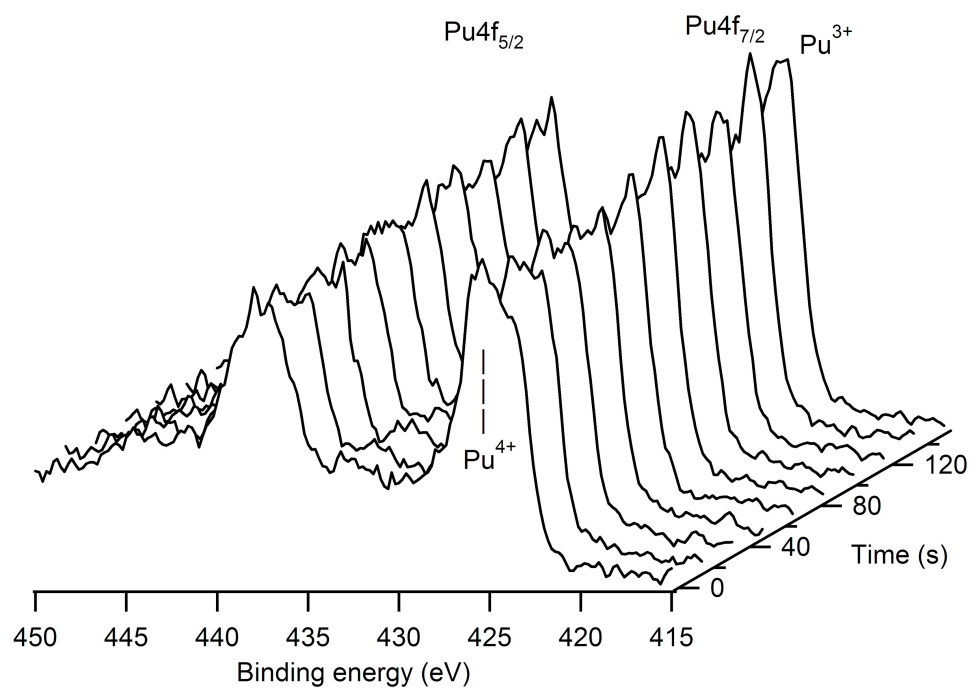


Figure 5